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These experimental results have furnished an initial understanding of the relationship between the thermal properties and microdomain structure of polyurethane elastomers.

OFFICE OF NAVAL RESEARCH FINAL TECHNICAL REPORT

FOR

Period 07-01-84 to 06-30-86

Contract N00014-84-K-0534

STRUCTURE-PROPERTY CHARACTERIZATION IN SEGMENTED POLYURETHANE BLOCK COPOLYMERS

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Jeffrey T. Koberstein

Princeton University
Polymer Materials Program
Department of Chemical Engineering
Princeton, NJ 08544

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This final project report describes reasearch that was performed during the past two years at Princeton University. The principal investigator is presently completing the original proposed research at the University of Connecticut in the Institute of Materials Science. For this reason the report is limited to describing the first two years of initial program results.

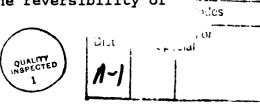
The project addresses the development of quantitative structure-property relationships for segmented polyurethane To this end, a number of sophisticated elastomers. The first characterization techniques have been applied. two papers that appeared in print1,2, discussed the use of solid state deuterium NMR spectroscopy to probe for the extent of microphase mixing in polyurethane elastomers, and characterize motions the in pure hard segment to For materials prepared from 4,4'-diphenyl materials. methane diisocyanate, butanediol, and polyoxyethylene end-capped polyoxypropylene soft segments, the following conclusions were reached: (1) the motions of the core of hard segment microdomains are identical to those of the pure hard segment material; (2) the amount of interfacial material quantified by NMR is in good agreement with that estimated from small angle x-ray scattering(SAXS); (3) the interfacial motions hard segments are rapid and isotropic, suggesting that interurethane hydrogen bonds are

short-lived in the interfacial regions.

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NMR was also applied to compare the motional behavior and non-crystalline polyurethane hard crystalline In the semicrystalline material, two clean discernable the distribution of in components are relaxation times, while only a single broad distribution is observed for the non-crystalline hard segment. The results also demonstrated that the predominant motion of the alkyl extender is a gauche-trans conformational chain consistent with the existance of kinked rather than extended conformations in the chain extender.

a third manuscript, Fourier transform infrared spectroscopy (FTIR) was used to examine the influence of transitions on hydrogen bonding³. morphological previous publications we had used differential scanning calorimetry (DSC) and simultaneous SAXS/DSC experiments to demonstrate the existance of order-disorder transitions at in the range of $170-190C^{4,5}$. temperatures The FTIR novel in that they were the first experiments were simultaneous FTIR/DSC experiments to be performed. results clearly reflected the onset of the order-disorder transition seen in earlier measurements as a decrease in the hydrogen bonding index. The technique also revealed that chemical changes occur during a DSC thermogram as evidenced by the emergence of an isocyanate band at high The band appears due to the reversibility of temperatures.



the urethane reaction.

Several manuscripts are currently being prepared based upon recent work. In particular, real-time diffraction and SAXS experiments have been performed to study the kinetics of crystallization and phase separation; simultaneous SAXS/DSC and WAXD/DSC experiments have elucidated the origins of multiple endotherms; comparison of these results with measurements of thermo-mechanical properties have furnished an understanding of the factors that control softening behavior; and finally a method for the estimation of phase compositions has been developed based on the combination of information garnered from SAXS and DSC analysis.

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Student Support

To date, the contract has provided support for two graduate students: Mr. A. Galambos, who is scheduled to complete his PhD degree during the next year, and Mr. W. Stockton, who is currently completing a Masters degree.

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